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Ogirigbo, OR and Black, L orcid.org/0000-0001-8531-4989 (2019) The effect of slag composition and curing duration on the chloride ingress resistance of slag-blended cements. Advances in Cement Research, 31 (5). pp. 243-250. ISSN 0951-7197

https://doi.org/10.1680/jadcr.17.00152

Accepted manuscript doi:
10.1680/jadcr.17.00152

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Accepted manuscript doi: 10.1680/jadcr.17.00152

Submitted: 23 August 2017

Manuscript title: The effect of slag composition and curing duration on the chloride ingress resistance of slag blended cements

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Abstract

This paper reports the influence of varying curing durations on the chloride ingress resistance of slag blends. Samples were prepared by combining two slags (S1 and S2), with a CEM I 52.5R at 30%. Mortar samples were cured for either 7 or 28 days, before being exposed to a 3% NaCl solution. Samples were subjected to two chloride exposure conditions (either complete submersion or a cyclic 6 hour wetting and drying cycle). Depths of free chloride penetration as well as total and water-soluble chloride contents were measured for the exposed samples. Samples cured for 28 days before exposure showed far better resistance to chloride ingress than those cured for 7 days. In terms of slag composition, slag 1 having an alumina content of 12.23% performed better than slag 2 of alumina content 7.77%, especially for samples cured for 7 days. This was attributed to the higher basicity of slag 1. However, when the samples were cured for 28 days, the difference between the performances of the slag blends became minimal. Despite this, the overall performance of the slag blends, which was compared against a CEM I 42.5R-type cement, was seen to be better at both curing durations.

1. Introduction

Over the recent years, it has become common practice to use supplementary cementitious materials (SCM) as partial replacement for Portland cement (PC) in the making of concrete. These SCMs are cheaper than PC and help to reduce the environmental footprint associated with concrete. They have also been shown to improve the technical performance of concrete. There are a wide range of SCMs in use, including fly ash, silica fume, metakaolin and ground granulated blast furnace slag (GGBS).

Several studies (Wan et al., 2004; Ballim and Graham, 2009; Chen et al., 2012; Güneyesi and Gesoğlu, 2008; Ben Fraj et al., 2012; Sengul and Tasdemir, 2009; Maes and De Belie, 2014; Divsholi et al., 2014) concerning the use of GGBS as a SCM in concrete production have shown that it improves the workability, long-term strength, thermal performance, and resistance to chemical attack from aggressive environments. Lower values of chloride diffusion coefficient and longer corrosion initiation times have been reported for concretes made from cement-slag blends. This has been largely attributed to a combination of the reduced permeability due to pozzolanic reactions, and to the high alumina content of the slags, which enables them to bind more of the chlorides in the form of Friedel's salt (Dhir et al., 1996; Cheng et al., 2005; Luo et al., 2003; Thomas et al., 2012; Khan et al., 2016; Galan and Glasser, 2015).

Recently, studies (Whittaker et al., 2014; Otieno et al., 2014; Whittaker et al., 2016; Ogirigbo and Black, 2016; Ogirigbo and Black, 2017; Ukpata et al., 2017) are beginning to look at the impact of chemical composition of GGBS on its performance as a cementitious material. This is because the chemical composition of GGBS is not fixed and can vary depending on the nature of the ore, type of iron or steel being produced and the composition of the limestone flux (Black, 2016). Thus a change in chemical composition is likely to impact on the performance of slag blends, especially in chloride environments. Otieno also showed that particle fineness, as well as slag composition, can impact on the chloride ingress resistance of slag blends (Otieno et al., 2014). Meanwhile, recent work has shown that the impact of slag composition on the performance of slag blends in chloride environments depended on the exposure temperature (Ogirigbo and Black, 2017). In all of these studies, the samples used for the chloride ingress experiments were cured for 28 days before they were exposed to the chloride environments. Several studies (Detwiler et al., 1994; Güneyisi and Mermerdaş, 2007; Chen et al., 2012; Shi et al., 2012; Ramezanianpour and Malhotra, 1995) have shown that samples cured for longer periods in water at a temperature of about 20℃ exhibit good chloride resistance. However, very few studies have looked at the impact of using shorter curing durations. This may be pertinent for slag blended cements due to the slow hydration of the slag. This paper has looked at how shorter curing durations can impact on the chloride ingress resistance of slag blends of different chemical compositions. This is significant, as in the UK, the minimum curing duration for CEM II is about 3 days (BS8110-1:1997), and usually in practice, formworks are often removed from concrete structures as early as 7 days or less.

2. Materials and methods

2.1 Materials

Two CEM I cements (42.5 R and 52.5 R) – designated as C1 and C2 respectively, were used for the study. C2 was replaced partially by 30 per cent by weight of GGBS. Two slags (S1 and S2) with similar physical properties yet different chemical compositions were used. C1 was used for the purpose of comparison because, in normal practice, blends are usually prepared with CEM I 52.5R to produce materials with similar performance to CEM I 42.5. The chemical composition of the cementitious materials, as obtained by XRF, is shown in Table 1, while Table 2 shows the physical properties of all the cementitious materials.

The fine aggregate used for the study complied with the specification for fine aggregates as given in (EN12620:2002+A1). The particle size ranged from 0.063 mm to 4 mm.

2.2 Details of mixes and curing conditions

Mortar samples were prepared from three sets of mixes – C1, C2S1 and C2S2, as shown in Table 3. Mixing was done using a Hobart-type mixer, according to the specifications given in (EN196-1:2005) for the preparation of mortar samples. Two sets of samples were cast; 40 x 40 x 160 mm prisms and 50 mm cubes. The prisms were used for total and water-soluble chloride content determination, while the cubes were used for chloride penetration tests. All samples were cured and tested at 20°C.

2.3 Details of exposure condition

The mortar samples were cured for either 7 or 28 days before they were exposed to two different laboratory-modelled chloride exposure conditions, described as follows:

- Saturated or submerged chloride exposure: This exposure condition is similar to the XS2 exposure classification as defined in (BS6349-1:2000) for chlorides. The samples were submerged in 3% NaCl solution (~0.53M NaCl), for a period of 90 days. The solutions were renewed every 4 weeks to maintain the salinity of the solution, and the liquid to solid ratio was kept above 12.5 millilitres per square centimetre of exposed surface, as specified in (EN12390-11:2015).

- Cyclic chloride exposure: This exposure condition is similar to the XS3 exposure classification as defined in (BS6349-1:2000) for chlorides. The samples were subjected to continuous cycles of wetting and drying. A cycle consisted of 6 hours of wetting during which the samples were submerged in a 3% NaCl solution, followed by 6 hours of drying. This cycle was chosen because it represents the daily application of salts that a reinforced concrete structure will be subjected to in a tidal zone (Ben Fraj et al., 2012). The top of the exposure chamber was left opened during the cyclic chloride exposure (as seen in Figure 1), to enable the samples dry under air, during the drying cycle. Although, carbonation was not avoided during drying, in the parent study where the mortar samples were checked for carbonation at the end of the cyclic chloride exposure, they were observed not to have undergone any form of carbonation. A schematic of the setup for this exposure condition is shown in Figure 1. A full description of the operating principles of the setup can be seen from (Ogirigbo, 2016).

2.4 Test methods

The depth of chloride ion penetration was determined using the silver nitrate (0.1M $AgNO_3$) spray technique, as used previously (Ogirigbo and Black, 2017; Elfmarkova et al., 2015). 50 mm mortar cubes were exposed to a 3% NaCl solution following initial curing for 7 or 28 days. The samples were subjected to the two chloride exposure conditions previously described. Samples were withdrawn from the chloride solution at 14, 28, 56 and 90 days, to determine the depths of chloride ion penetration.

Total chloride contents were determined using 40 x 40 x 160 mm mortar samples. A full description of how the samples were prepared and conditioned before being submerged in the chloride solution can also be found elsewhere (Ogirigbo and Black, 2017). The mortar samples were submerged for a period of 90 days, after which layers were extracted from the sample by dry cutting. A total of 7 layers (approximately 5 mm thick) were cut from each sample. Each layer was ground so as to pass through a 300 micron sieve, and stored separately in polythene bags before testing. Total chloride content was determined for each layer using the procedure recommended by (RILEM, 2002a). 50 ml of conc. HNO_3 was poured into a beaker containing 1 gram of the dried sample. After the effervescence had stopped, the mixture was heated and allowed to boil for about 1 min. Thereafter, 5 ml of 0.1M $AgNO_3$ was added. The resulting solution was filtered under vacuum and made up to a volume of 200 ml by adding diluted HNO_3. This was titrated against a 0.05M ammonium thiocyanate solution (NH_4SCN). A blank test was also run using the same procedure outlined above, but without any sample. The total chloride content per mass of the dried sample was determined using the expression below:

$$\%Cl = \frac{3.5453 V_{Ag} M_{Ag} (V_2 - V_1)}{m V_2} \quad (1)$$

where:

V_{Ag} volume of $AgNO_3$ added in cm^3

M_{Ag} molarity of the $AgNO_3$ solution

V_1 volume of NH_4SCN used in the sample in cm^3

V_2 volume of NH_4SCN used in the blank test in cm^3

m mass of the dried sample used for the test in grams

The average total chloride content obtained per layer from three measurements was plotted against the distance of the centre of each layer from the exposed face, to obtain total chloride profiles. The non-steady state chloride diffusion coefficient D_c and the chloride content at the surface C_s were determined by performing a non-linear regression analysis on the total chloride profiles, using the expression below (EN12390-11:2015):

$$C_x = C_s\left(1 - erf\left[\frac{x}{2\sqrt{D_c t}}\right]\right) \tag{2}$$

where:

C_x	chloride content measured at average depth x and exposure time t, % by mass of sample
C_s	calculated chloride content at the exposed surface, % by mass of sample
x	depth below the exposed surface to the mid-point of the ground layer, in metres
D_c	calculated non-steady state chloride diffusion coefficient, in square metres per second (m^2/s)
t	exposure time, in seconds (s)
erf	error function

The regression analysis was done using Excel solver function. The first set of data (the chloride content of the first layer, obtained very close to the exposed surface) were not included in the regression analysis as recommended in (EN12390-11:2015).

In determining the water-soluble chloride content, which is defined as the amount of chloride ion in a concrete specimen which can be leached out by water at room temperature (RILEM, 2002b), 5 grams of ground sample were taken from each layer of the same samples used for total chloride content determination. This material was placed in a plastic bottle, and 100 ml of distilled water was added (a solid to liquid ratio 1:20) (Arya et al., 1987), before the plastic bottle was sealed and left to stand for 72 hours at 20°C. At the end of the standing period, the solution was filtered off and the chloride concentration of the filtrate was determined by ion chromatography. The water-soluble chloride content, which was taken as the chloride concentration of the filtrate, was expressed in parts per million (ppm) and plotted against the distance of the centre of each layer from the exposed face, to obtain the water-soluble chloride profile.

3. Results and discussion

3.1 Depth of chloride penetration

3.1.1 Saturated or submerged chloride exposure

Figure 2 shows the free chloride penetration depths measured on samples that were cured and exposed under saturated conditions. The effect of curing duration on the depth of chloride penetration can be seen by comparing Figure 2a to 2b. The penetration depths for all samples following 7 days' curing were significantly greater than after 28 days' curing. Differences could also be seen in the extent of chloride penetration as a function of exposure time. Samples cured for only 7 days before exposure showed a continual increase in chloride penetration with time. Meanwhile samples cured for 28 days showed chloride ingress over the first 28 days' of exposure, but very little beyond that. This agrees with previous studies that have shown that longer curing duration in water enhances the chloride ingress resistance of concretes (Detwiler et al., 1994; Güneyisi and Mermerdaş, 2007; Chen et al., 2012; Shi et al., 2012; Ramezanianpour and Malhotra, 1995). The reason for the significant decrease in the chloride penetration depths of the 28 days pre-cured samples can be attributed to two factors; capillary porosity and chloride binding.

In the parent study (Ogirigbo, 2016), capillary porosity was measured for paste samples prepared from these mixes. The results obtained (see Table 4) showed a drop in the capillary porosity of about 1.9 percentage points for the C1 mix and by over 5.2 percentage points for the slag blends, when the curing duration was increased from 7 to 28 days. This implies that the samples cured for 28 days had a finer pore structure and was more resistant to the ingress of chloride ions. Furthermore, the coarse capillary porosity was lower for the slag blend containing the more basic, and therefore, more reactive slag 1.

Concerning chloride binding, several studies (Lothenbach et al., 2007; Escalante-García and Sharp, 1998) have shown that this is related to the degree of hydration of the cementitious materials. In particular, chlorides are known to bind to C-S-H (Florea and Brouwers, 2012), of which more is present when the samples have hydrated to a greater degree, such as in the samples cured for 28 days (Ogirigbo and Black, 2016). Thus, more chlorides were bound by the 28 day cured samples, resulting in lower free chloride penetration depths.

In all instances, the chloride penetration depths measured for the slag blends were much lower than that of the plain CEM I 42.5R mix. This is despite the higher porosities at 7 days (Table 4). This can be attributed to the higher chloride binding capacities of the slag blends due to their higher alumina contents. Several studies (Dhir et al., 1996; Cheng et al., 2005; Luo et al., 2003; Thomas et al., 2012; Ogirigbo and Black, 2017) have shown that the higher the alumina content of a binder, the greater its chloride binding capacity. For the slag blends, C2S1 showed better resistance to chloride ion penetration than C2S2, especially for samples that were cured for 7 days prior to exposure. This agrees with the results obtained elsewhere (Otieno et al., 2014), and can be attributed to the higher alumina content and lower porosity of slag 1 as seen in Table 1 and Table 4 respectively. For the slag blends cured for 28 days before exposure, there was minimal difference in the chloride penetration depths, especially at later ages. This implies that the impact of prolonged curing was more significant for the less basic, lower alumina slag 2 blend. Prolonged curing helped to offset the lower reactivity of this slag.

3.1.2 Cyclic chloride exposure

Figures 3a and 3b shows the depth of free chloride penetration for samples that were subjected to a cyclic chloride exposure of 6-hr wetting in a 3% NaCl solution followed by 6-hr drying. The two figures show data obtained after initial curing under water for 7 and 28 days respectively.

As observed in the saturated chloride exposure (shown in Figure 2), samples cured for 28 days (Figure 3b) had fewer chlorides than those that were cured for 7 days (Figure 3a). Comparing Figure 2a to Figure 3a, it can be seen for the 7 days pre-cured that the exposure profile did not have any significant impact on the depth of chloride penetration. It is proposed that these samples allowed rapid ingress, so capillary suction was less important.

For the 28 days pre-cured samples, it was observed that samples subjected to cyclic chloride exposure (Figure 3b) had greater chloride ingress than those exposed to saturated conditions (Figure 2b). This was especially true for the C1 samples. The reason for this as observed also by (Ben Fraj et al., 2012; Otieno et al., 2016), can be attributed to the combined effect of diffusion and capillary suction. For unsaturated concrete exposed to alternate wetting and drying cycles, the chlorides diffuse into the concrete during the wetting period by concentration gradient. In the drying period, only water evaporates from the concrete surface while the salts remain in the concrete leading to an accumulation of chlorides (Ben Fraj et al., 2012), which then increases capillary suction (Hong and Hooton, 1999; Nielsen and Geiker, 2003; Oh and Jang, 2007).

From Figures 2 and 3, it can be seen that the slag blends performed better than the plain C1 mix, particularly following cyclic chloride exposure. Also, as observed in the saturated chloride exposure, the slag 1 blend performed better than the slag 2 blend, but only for the samples that were cured for the shorter duration of 7 days.

3.2 Total and water-soluble chloride content

Figures 4 and 5 show total and water-soluble chloride profiles obtained for samples cured for either 7 or 28 days before being immersed completely in a 3% NaCl solution for a period of 90 days.

As seen in Figure 4, while there were similarities in the total chloride contents of all samples at their surfaces, differences between the C1 samples and slag blends became evident at depth. Chloride contents decreased rapidly with depth, particularly for the slag blends, and to a lesser extent following longer curing prior to immersion. The total chloride profiles reflect the difference in sample porosity, indicating the lower porosity of slag blends, and the benefits of prolonged curing. This was also observed in Figure 5 and agrees with the chloride penetration results shown in Figures 2 and 3, where it was seen that the depth of chloride penetration into samples cured for 28 days were lower than those that were cured for 7 days before exposure.

Comparing Figures 2 and 4, it can be seen that the difference between the total chloride contents of the samples cured for 7 and 28 days (Figure 4) is not as significant as the difference between the depths of chloride penetration measured for these samples (Figure 2). The reason for this is seen in Figure 5, which shows the water-soluble (free) chloride content obtained from the same samples used for the determination of the total chloride content. In Figure 5, we see a clear difference in the free chloride content of the samples cured for 7 days compared to those pre-cured for 28 days before exposure, especially at the region close to the exposed face. This can be attributed to chloride binding. The samples cured for 28 days before exposure exhibited higher degrees of hydration (Ogirigbo, 2016) and were able to bind more of the chlorides, hence their lower free chloride content. The results shown in Figure 5 correlates with those shown in Figure 2, and thus confirms the benefit of prolonged curing on the resistance to the ingress of free chloride ions.

3.3 Chloride diffusion coefficient (D_c)

Table 5 shows the chloride diffusion coefficient (D_c) and the chloride concentration at the surface (C_s) obtained by a non-linear regression fit of Fick's 2nd law of diffusion to the total chloride profiles shown in Figure 4.

The D_c values of the samples cured for 28 days were lower than those cured for 7 days before exposure. However, the trend was reversed for the values of C_s. This can be attributed to the finer pore structure preventing chloride ion ingress, coupled with higher chloride binding capacity of the 28 days cured samples. This would lead to an accumulation of chloride ions at the region close to the exposed face, resulting in the higher values obtained for C_s. Looking at the shape of the total chloride profiles, samples were cured for 28 days showed more rapidly diminishing chloride contents with depth. Such profiles have been reported for concrete mixes with high chloride binding capacities (Tang, 1996).

The plain cement mix (C1) showed higher diffusion coefficients than the slag mixes. Similar results were also reported by (Ma et al., 2016; Maes et al., 2013). Comparing the two slag blends, the D_c values of C2S1 were lower than those obtained for C2S2 at both curing durations, with the difference being more significant for the samples that were cured for shorter durations. This agrees with the results of the chloride penetration depth for both exposure conditions as shown earlier (Figures 2 and 3), and indicates that the longer curing duration of 28 days was more beneficial for the less basic, lower alumina content blend.

4. Conclusion

This study has looked at the influence of varying curing durations on the chloride ingress resistance of slag blends. Irrespective of the binder type, samples cured for longer periods were seen to perform much better in resistance to water and chloride ingress than those cured for shorter periods. Two reasons are given for this. Firstly, the samples cured for longer prior to exposure showed higher degrees of hydration and thus lower porosities. Secondly, chloride binding was greater in the samples cured for longer periods.

The slag blends showed better resistance to chloride ingress than the reference cement, which was a CEM I 42.5R-type cement. This was attributed to a combination of their lower porosities inhibiting chloride ingress, and to their higher alumina contents enabling greater chloride binding. In comparing the performance of both slag blends, slag 1 having an alumina content of 12.23% performed better than slag 2 of alumina content, 7.77%. However, the difference in performance between the slag blends was only observed to be significant for the samples that were cured for shorter durations – where there was a greater difference in porosity. When the samples were cured for longer durations, the difference in alumina content of the slags did not seem to have any significant impact on their resistance to chloride ingress. This implies that for slags, reactivity (and hence porosity) is perhaps more important than alumina content.

Overall, the results of this study show that for good performance of slag blends in chloride environments, longer curing durations are essential. However, if shorter curing durations are to be adopted, as often seen in practice, then to achieve good early performance, more basic slags richer in alumina should be used in preparing the blends.

Acknowledgements

The authors would like to thank the Petroleum Technology Development Fund (PTDF) of Nigeria for providing the funds for this research.

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Table 1: Chemical composition of cementitious materials

	SiO_2	Al_2O_3	CaO	MgO	SO_3	TiO_2	Fe_2O_3	K_2O	Na_2O	MnO
C1	19.71	5.08	63.16	2.19	2.97	0.26	2.97	1.08	0.06	0.03
C2	19.10	5.35	62.38	2.37	3.34	0.25	2.95	1.05	0.05	0.03
S1	36.58	12.23	38.24	8.55	1.00	0.83	0.48	0.65	0.27	0.64
S2	40.14	7.77	37.9	9.51	1.47	0.30	0.78	0.55	0.36	0.64

Table 2: Physical properties of cementitious materials

Property	Unit	C1	C2	S1	S2
Density	g/cm^3	3.23	3.18	2.94	2.95
Blaine	cm^2/g	3510	5710	4490	4090
Particle size, d10	µm	-	-	3.1	3.3
d50	µm	-	-	11.0	11.9
d90	µm	-	-	47.0	42.4

Table 3: Mix ratios (by weight) for the mortar specimens

Mix	w/b	C1	C2	Slag 1	Slag 2	Water	Fines
C1	0.5	1	0	0	0	0.5	3
C2S1	0.5	0	0.7	0.3	0	0.5	3
C2S2	0.5	0	0.7	0	0.3	0.5	3

Table 4: Effect of curing duration on capillary porosity determined by SEM-BSE image analysis [taken from (Ogirigbo, 2016)]

Mix	Porosity (%)	
	7 days	28 days
C1	9.0 ± 0.16	7.1 ± 0.13
C2S1	11.8 ± 0.10	6.5 ± 0.11
C2S2	12.3 ± 0.12	7.0 ± 0.07

Table 5: C_s and D_c of the slag blends obtained by non-linear regression fit of Fick's 2nd law of diffusion to the total chloride profile of all the mixes

		C_s (% mass of dried sample)	D_c (m^2s^{-1})	Adj. R^2
7 days pre-cured	C1	0.38	5.15×10^{-11}	0.9135
	C2S1	0.44	5.41×10^{-12}	0.9796
	C2S2	0.47	7.70×10^{-12}	0.9816
28 days pre-cured	C1	0.50	1.75×10^{-11}	0.9980
	C2S1	0.55	3.87×10^{-12}	0.9936
	C2S2	0.58	4.00×10^{-12}	0.9916

Figure 1: Schematic of the setup for the cyclic chloride exposure

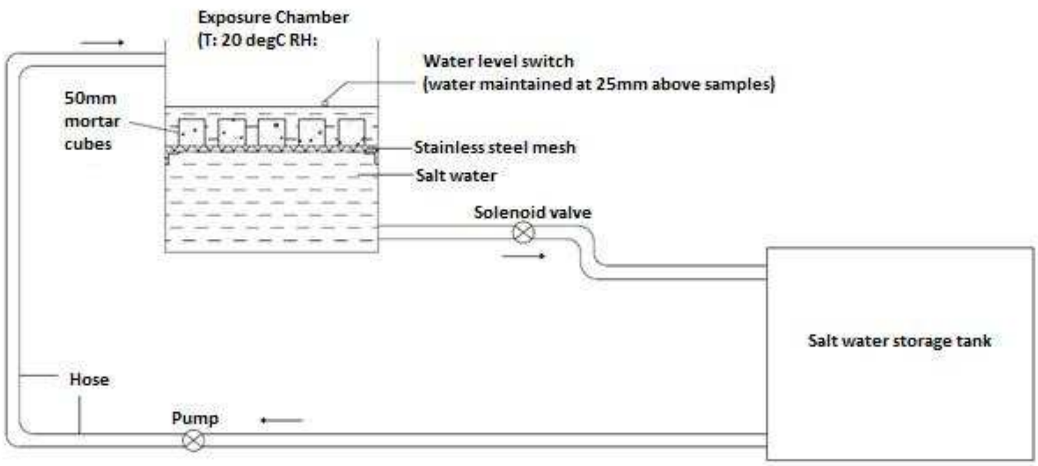
Figure 2: Depth of free chloride penetration for samples continuously submerged in chloride solution (a) samples cured for 7 days before exposure (b) samples cured for 28 days before exposure

Figure 3: Depth of free chloride penetration for samples subjected to a cyclic chloride exposure of 6-hr wetting in a 3% NaCl solution followed by 6-hr drying (a) samples cured for 7 days before exposure (b) samples cured for 28 days before exposure.

Figure 4: Total chloride profiles for samples cured for (a) 7 days and (b) 28 days before ponding in a 3% NaCl solution for 90 days

Figure 5: Water-soluble chloride profiles for samples cured for (a) 7 days and (b) 28 days before ponding in a 3% NaCl solution for 90 days

Figure 1


Exposure Chamber
(T: 20 degC RH:
Water level switch
(water maintained at 25mm above samples)
50mm
mortar
cubes
Stainless steel mesh
Salt water
Solenoid valve
Salt water storage tank
Hose
Pump

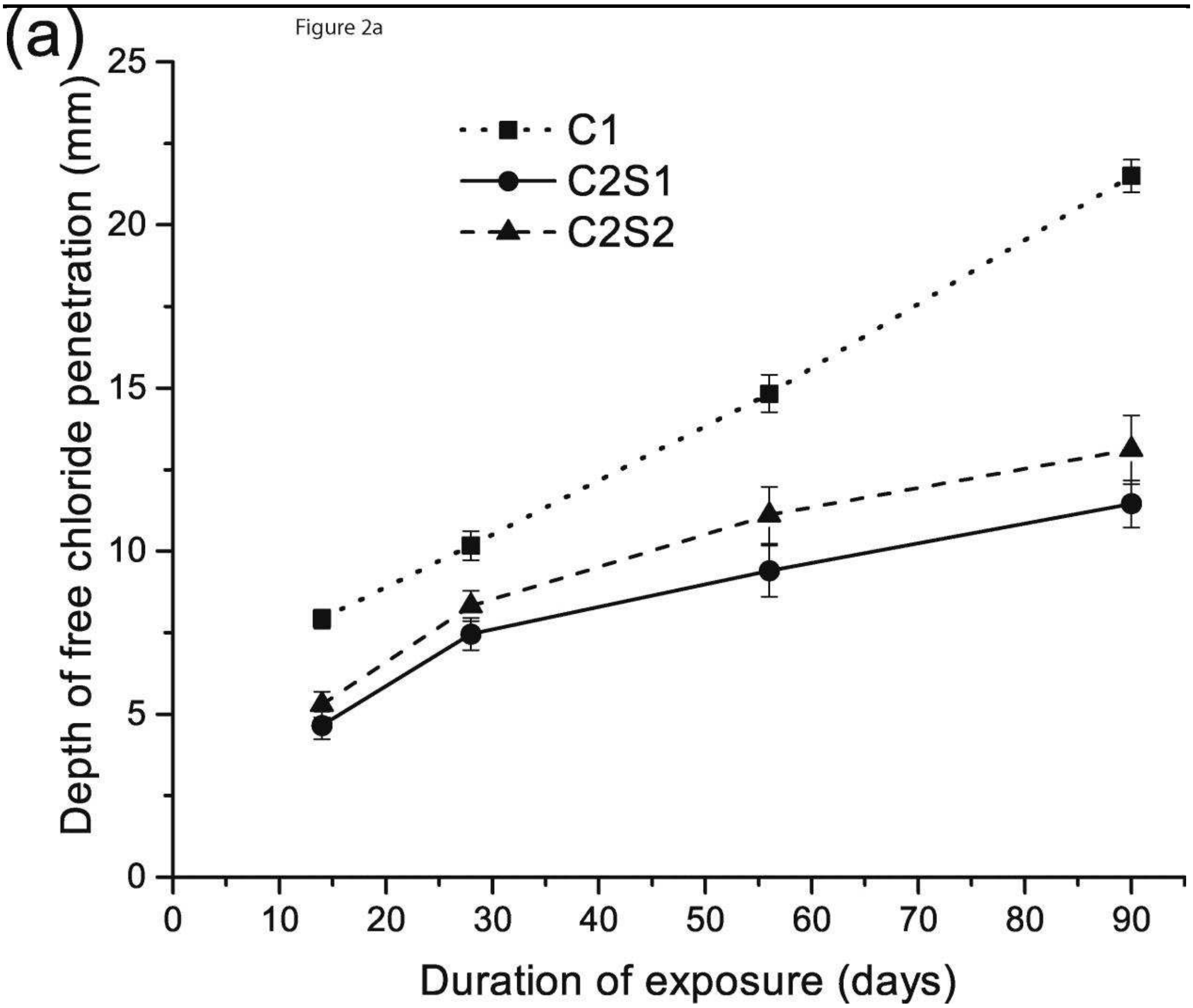

(a)
Figure 2a
C1
C2S1
C2S2
Depth of free chloride penetration (mm)
0
5
10
15
20
25
0
10
20
30
40
50
60
70
80
90
Duration of exposure (days)

Figure 2b

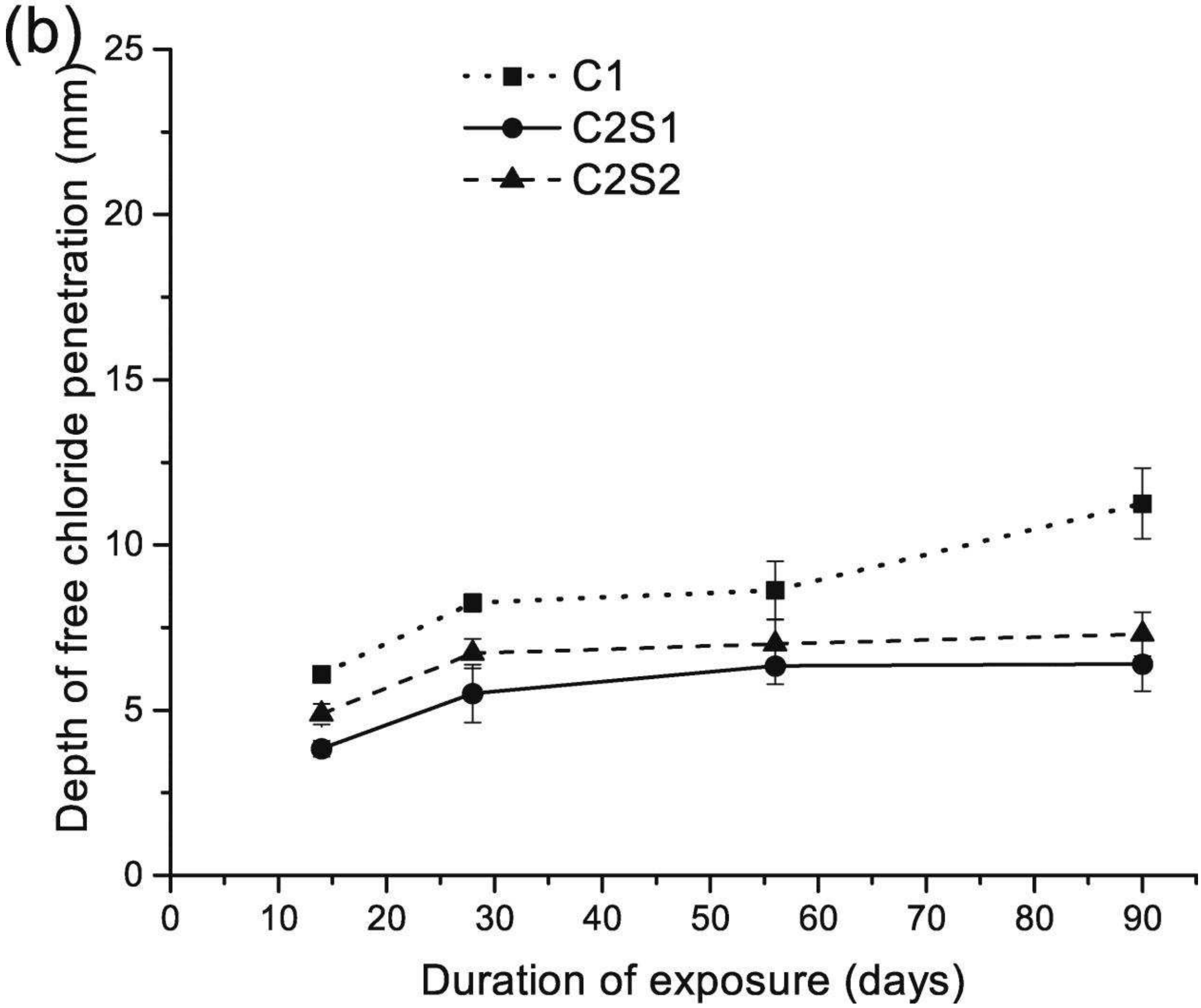

(b)
Depth of free chloride penetration (mm)
0
5
10
15
20
25
Duration of exposure (days)
0
10
20
30
40
50
60
70
80
90
C1
C2S1
C2S2

Figure 3a

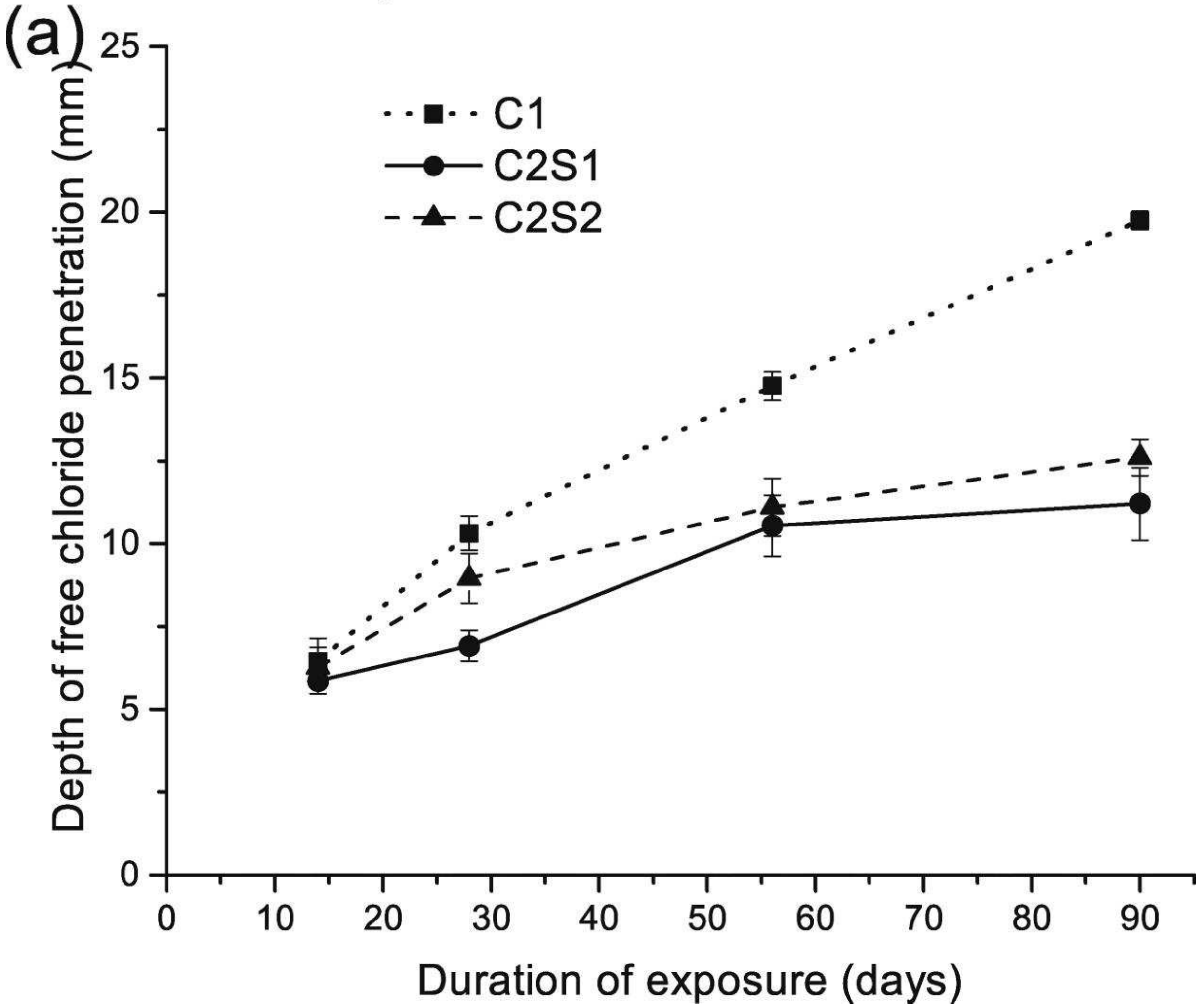

(a)
Depth of free chloride penetration (mm)
0
5
10
15
20
25
C1
C2S1
C2S2
0
10
20
30
40
50
60
70
80
90
Duration of exposure (days)

Figure 3b

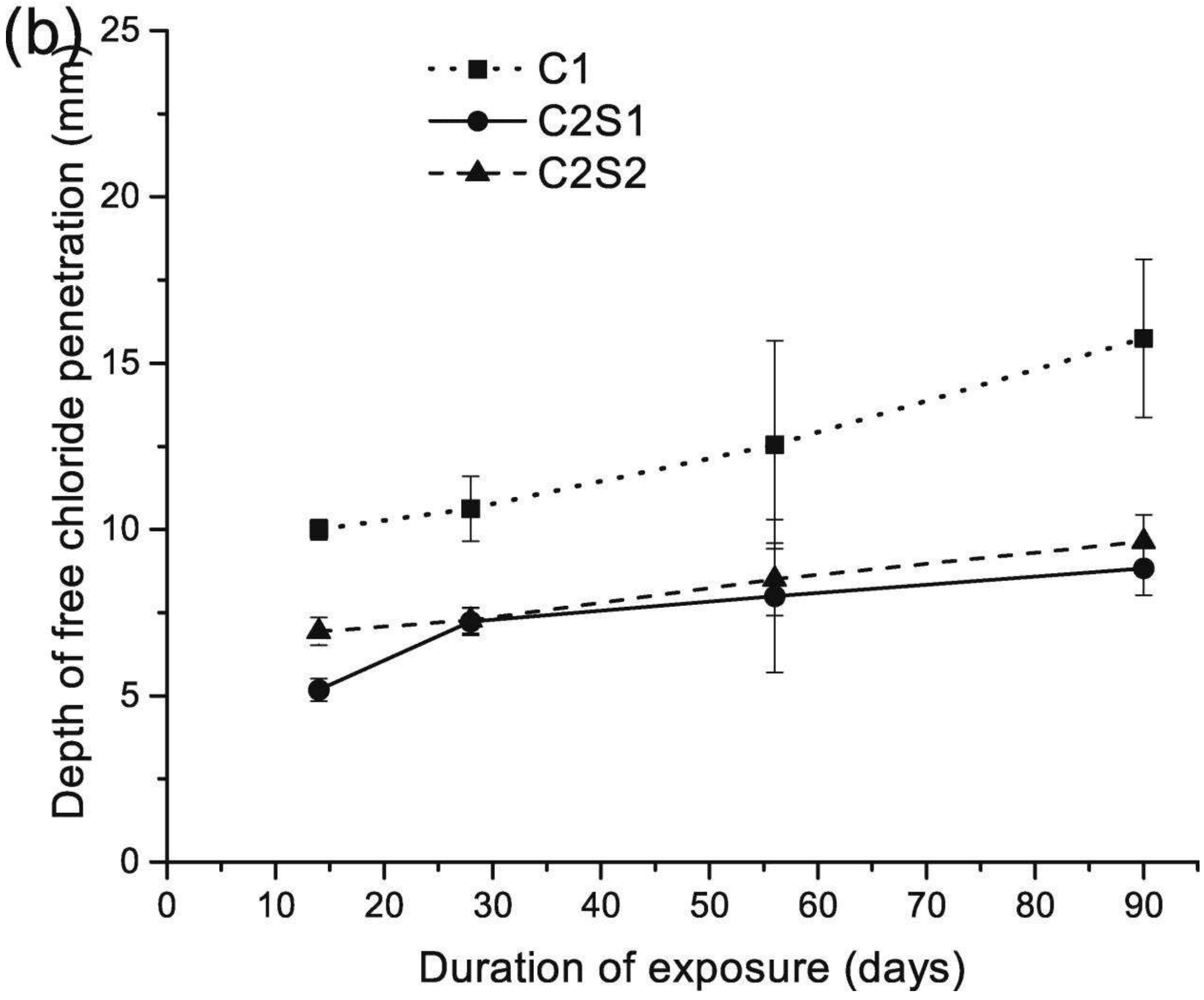

(b)
Depth of free chloride penetration (mm)
0
5
10
15
20
25
0
10
20
30
40
50
60
70
80
90
Duration of exposure (days)
C1
C2S1
C2S2

Figure 4a

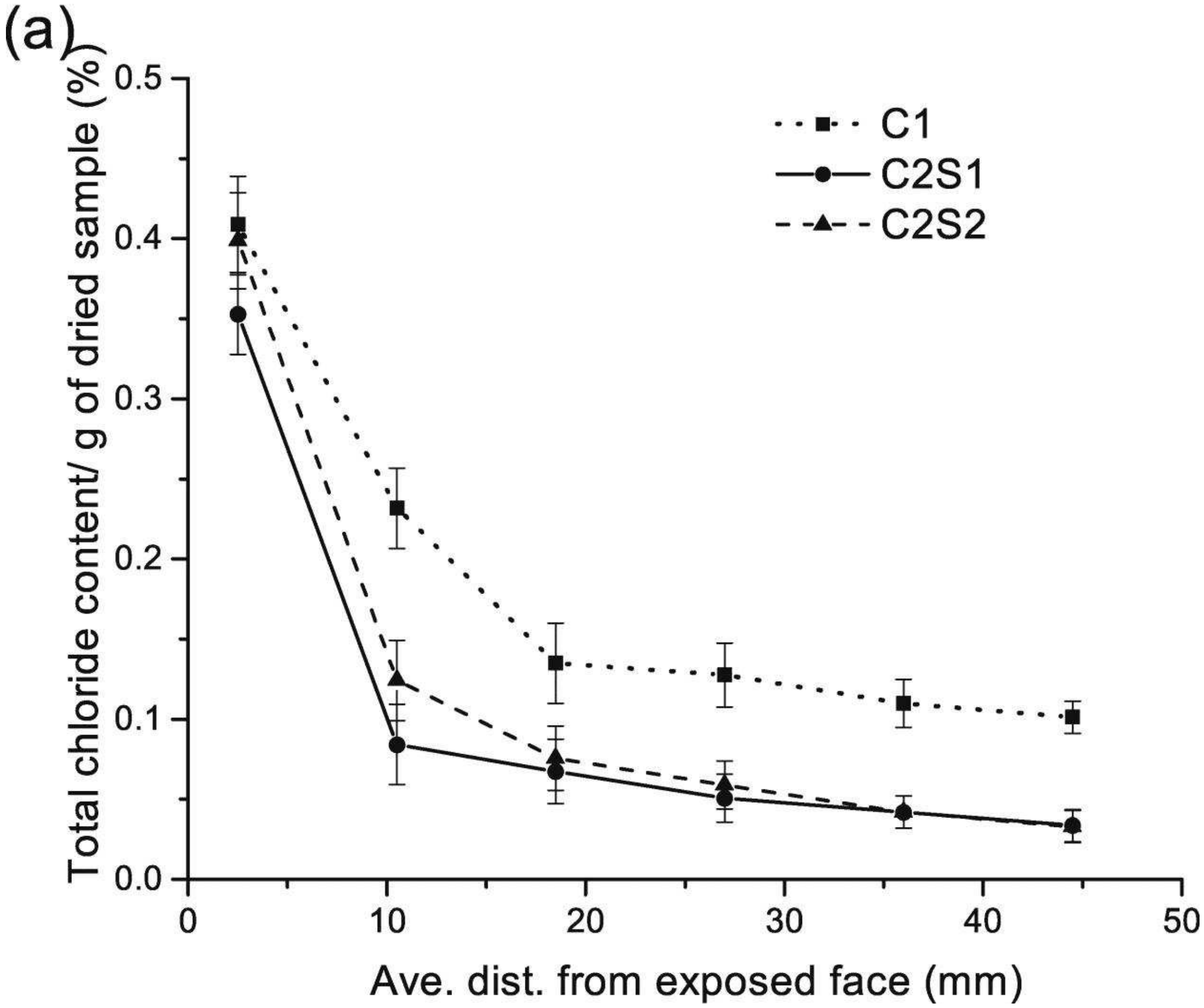

(a)
Total chloride content/ g of dried sample (%)
0.0
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50
Ave. dist. from exposed face (mm)
C1
C2S1
C2S2

Figure 4b

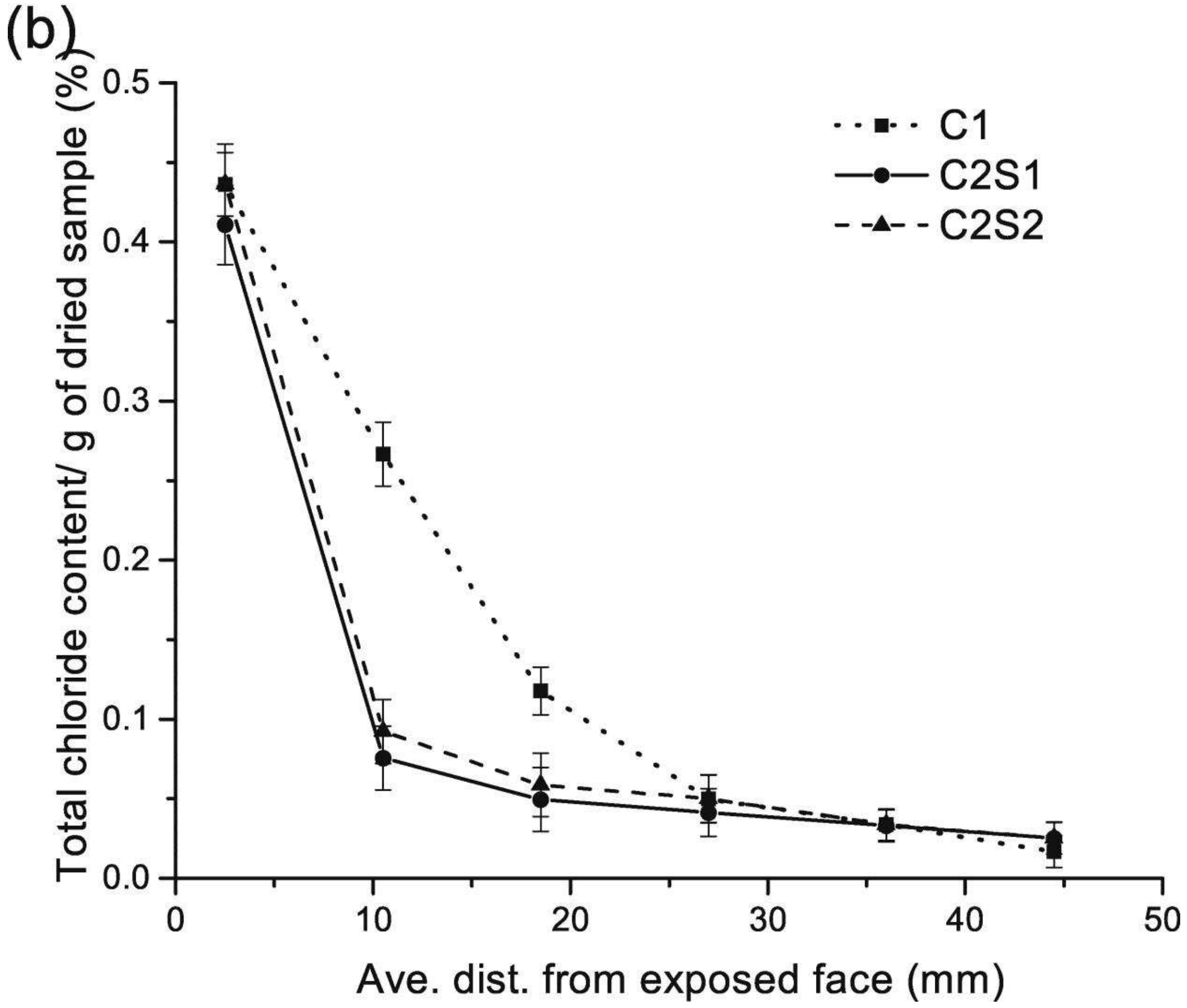

(b)
Total chloride content/ g of dried sample (%)
0.0
0.1
0.2
0.3
0.4
0.5
Ave. dist. from exposed face (mm)
0
10
20
30
40
50
C1
C2S1
C2S2

Figure 5a

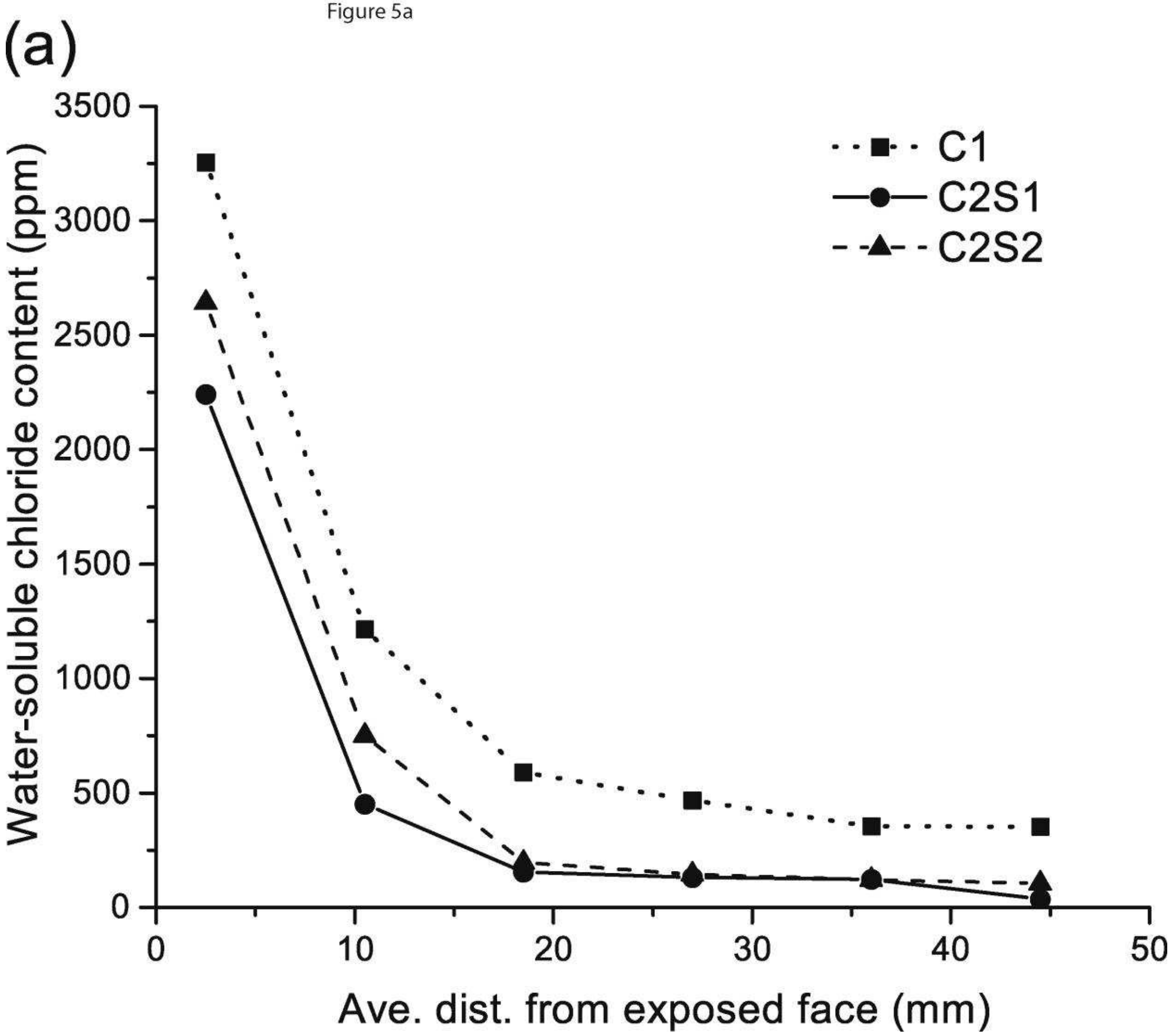
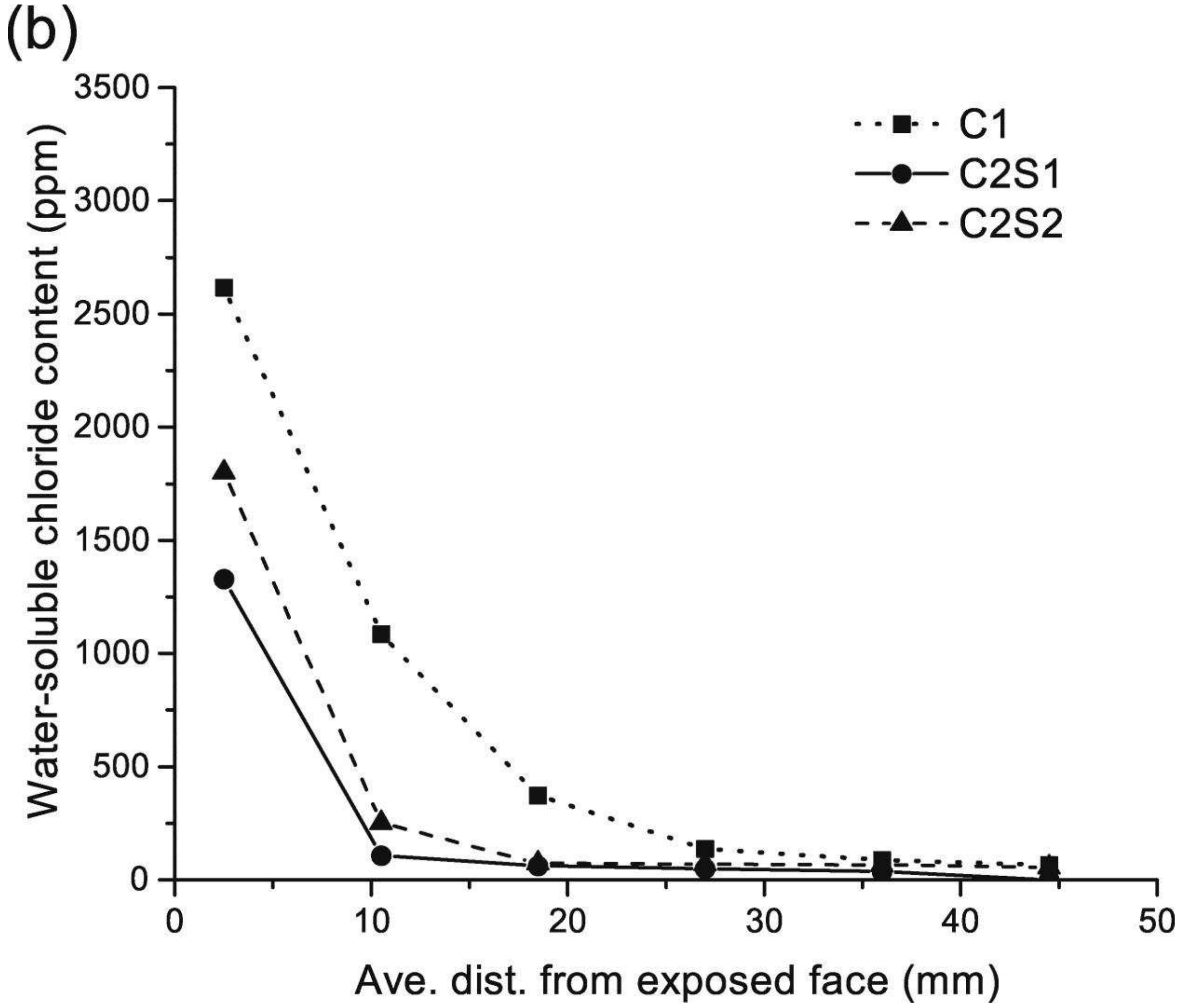

(a)
Water-soluble chloride content (ppm)
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
Ave. dist. from exposed face (mm)
C1
C2S1
C2S2

Figure 5b


(b)
Water-soluble chloride content (ppm)
0
500
1000
1500
2000
2500
3000
3500
Ave. dist. from exposed face (mm)
0
10
20
30
40
50
C1
C2S1
C2S2